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A review on hydrogen production using aluminum and aluminum alloys

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Abstract

The hydrogen economy has been identified as an alternative to substitute the non-sustainable fossil fuel based economy. Ongoing research is underway to develop environmentally friendly and economical hydrogen production technologies that are essential for the hydrogen economy. One of the promising ways to produce hydrogen is to use aluminum or its alloys to reduce water or hydrocarbons to hydrogen. This paper gives an overview on these aluminum-based hydrogen production methods, their limitations and challenges for commercialization. Also, a newly developed concept for cogeneration of hydrogen and electrical energy is discussed.

Keywords: Hydrogen production; Aluminum; Aluminum alloys; Water; Alcohols; Electricity cogeneration

Contents

1. Introduction

Due to fossil fuel depletion and air pollution arising from its combustion, there is an urgent demand for renewable, clean fuel alternatives for our future energy supply. Hydrogen, a regenerative and environmentally friendly fuel with high calorific value, has attracted much attention by scientists. The hydrogen economy concept envisions that the future global energy demands will be mainly satisfied by hydrogen fuel instead of fossil fuels [1]. For a successful transition to the hydrogen economy, hydrogen production should be well developed first so that the technology can be implemented in a sustainable, clean, and economical manner.

For certain metal reactants that can induce hydrogen evolving chemical reactions, aluminum and its alloys are recognized to be one of the most suitable metals applicable for future hydrogen production and there is a trend to utilize them as an energy material especially in recent years. In addition, the metal utilization is identified to be an effective, user-friendly, and safe approach for both hydrogen production and energy storage.

This paper aims to give an overview on the existing methods for producing hydrogen using aluminum and its alloys, their

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limitations, and the challenges for commercialization. These methods are classified into two categories, namely aluminum–water reactions and aluminum–alcohol reactions that reduce water and hydrocarbons, respectively, into hydrogen. Besides, the cogeneration of hydrogen and electrical energy, a relatively new promising concept, will be discussed in the subsequent section.

2. Current status of hydrogen production and storage

Although hydrogen is the most abundant element in the universe, elementary hydrogen gas is hardly found on earth [2]. It is therefore necessary to extract hydrogen from either water or hydrocarbons, both of which are abundant on earth. Existing hydrogen production is mainly based on biological processes, electrochemical water electrolysis, or chemical methods [3]. Taking into account the low conversion efficiencies of biological systems [4] as well as the high cost of water electrolysis [5], chemical methods dominate the market for commercial hydrogen production. Hydrogen can be chemically extracted from its sources by steam or partial oxidation reforming of natural gas, coal gasification, reforming of biomass, water photolysis, etc. At present, approximately 95% hydrogen is generated by steam/partial oxidation reforming of natural gas and coal gasification [6]. Although these techniques are mature and have the lowest costs, they cannot act as a long-term strategy for the hydrogen economy because the raw materials used are all based on fossil fuels, which are neither sustainable nor clean. Reforming of biomass, an abundant and renewable source, may be considered as a sustainable way to produce hydrogen but its carbon dioxide (CO_2) neutrality is still a controversial issue. Furthermore, this technique is seriously restricted by the low hydrogen yield and energy content of biomass [7]. Moreover, additional energy will be required for conversion of syngas into hydrogen through water–gas shift reaction [8]. The high cost for growing, harvesting, and transporting biomass is another disadvantage for biomass utilization [7]. Water photolysis, an advanced chemical technology regarded to be very promising, is still under development and some technical difficulties make it far from industrial applications [9].

Hydrogen storage is another important constituent for the development of the hydrogen economy. Although hydrogen has a high gravimetric energy density, its volumetric energy density is very low due to its low density. In addition, hydrogen is a flammable gas with ignition energy of only 0.03 mJ. That means even a static electricity discharge or an agitation of compressed or liquid hydrogen may generate sufficient energy to cause its ignition [10]. Thus, the technological development for compact and safe hydrogen storage has been a challenging task. To store more hydrogen for a given volume, conventional methods include high-pressure compression and low-temperature liquefaction. Although these two technologies are mature in today's industries, their applications to hydrogen storage are not totally safe and there are still many technical problems to be solved. Moreover, in terms of energy density stored, these two hydrogen storage methods are less competitive than conventional fuel storage tanks for gasoline and diesel [10]. Currently, hydrogen storage by use of chemical hydrides has received much attention and it offers a safe solid-state storage for hydrogen. However, the slow kinetics and high temperature required for hydrogen release impede the wide applications of hydrides [11]. Besides, hydrides are too costly [10]. At present, new storage technologies, such as the physisorption of hydrogen in porous structures, are also under development.

Recently, certain chemical reactions of reactive metals accompanied by hydrogen evolution have received increasing concerns in the field of hydrogen energy because of their potential applications in both hydrogen production and storage. In these reactions, the hydrogen sources such as water and hydrocarbons are usually used as one of the reactants, from which hydrogen will be extracted with the help of metals of high activity. This is in fact an innovative application of an old technology as hydrogen evolution through the displacement reactions of metals was discovered several centuries ago and some of these reactions have already been studied thoroughly. In certain metal reactions, a violent hydrogen release occurs soon after the contact between reactants even under mild conditions. They therefore make a real-time hydrogen production possible. The on-demand hydrogen release using metals can eliminate the need for hydrogen storage. For those scenarios, hydrogen is indirectly stored in the form of its original sources. Such systems can be more compact and much safer. It is noted that the hydrogen contents per unit volume in water (111 kg/m^3) and in gasoline (84 kg/m^3) are higher than that in the form of pure liquid hydrogen (71 kg/m^3) [10]. So far, studies have been performed on the use of metals including Zn, Mg, and Al to generate hydrogen [12–18]. Among the different metals, aluminum has been identified to be the most promising candidate for the purpose of hydrogen generation [19].

3. Use of aluminum and its alloys for hydrogen production

Aluminum and its alloys possess a number of valuable mechanical, electrical, and thermal properties. They are widely used in various fields, such as transportation, building, electrical engineering, as well as packaging. Noticing its high energy density of 29 MJ/kg [20], there is an increasing concern on using aluminum-based materials as an energy storage or conversion material in recent years. Being the most abundant crustal metal on the earth, which can be fully recycled, aluminum is regarded as a ‘‘viable metal’’, the utilization of which exactly coincides with today's theme of developing sustainable energy. Another advantage of aluminum is its light weight. With its low density of 2700 kg/m^3, aluminum is the lightest among all commonly used metals [21]. The density of its different alloys is in the range of 2600–2800 kg/m^3 [21]. Such a property helps to lead to a significant reduction in the total weight of a system.

One typical example of the use of aluminum in the energy field is its application in batteries. With strongly alkaline electrolyte (pH 14), the potential for the discharge reaction of pure aluminum can be as low as -2.33 V with respect to the

standard hydrogen electrode [22]. Also, the tri-valence of aluminum along with its light weight yields a high electrochemical equivalence of 2.98 Ah/g [23]. All these factors make aluminum a suitable anode material for hundreds of years. Li and Bjerrum [23] reviewed various aluminum batteries in detail. Particularly, the aluminum–air battery, composed of an aluminum-based anode, gas diffusion cathode, and aqueous alkaline (sometimes neutral) electrolyte, was reported to be the only battery system that provided the prospect of an electric vehicle with a range and a refueling time comparable to those of internal-combustion-engine vehicles [22].

Inspired by the hydrogen formation in some corrosion reactions of aluminum, many investigators began to focus their studies on using aluminum for the production of hydrogen. Since pure aluminum is a highly electronegative metal, it is susceptible to corrosion by changing into ion forms. Unlike other metals, the electrochemical corrosion of aluminum-based materials in some scenarios cannot be predicted using the Wagner–Traud mixed potential model due to the existence of the negative difference effect (NDE), i.e. the hydrogen evolution rate will increase with increasing anodic polarization [24]. The mechanisms behind the NDE phenomenon have not been fully understood yet. In practical uses, however, aluminum and its alloys are usually well protected by a dense oxide layer formed on their surface due to their strong affinity for oxygen, which shifts the corrosion potential of aluminum by nearly 1 V in the positive direction. Thus, aluminum-based materials are normally recognized to have good resistance to corrosion. Such a resistance can be a great advantage for the aluminum used as constructional materials; however, the resistance becomes the major hurdle to realizing continuous hydrogen generation through aluminum corrosion. The corrosion processes of aluminum are totally CO_2-free, with the by-products having minimal environmental impact. Aluminum oxide (Al_2O_3) and aluminum hydroxide ($Al(OH)_3$), formed through aluminum–water reactions, are very useful in water treatment, paper making, as well as fire inhibition. It is also possible to fully recover aluminum from Al_2O_3 through the Hall–Héroult process, which reduces the energy consumption compared with the primary aluminum production but costs more than the secondary aluminum production from direct aluminum recycling. Aluminum alkoxides, by-products of aluminum–alcohol reactions, are important catalysts in some industries. According to a life cycle assessment (LCA) conducted by Hiraki et al. [25] considering both the processes of the required deionized water production and residue treatment, the energy requirement of aluminum-based hydrogen production is only 2% and its carbon dioxide emission is 4% of conventional production methods. Aluminum and its alloys are very suitable for on-board vehicle hydrogen supply. A modern, commercially available electric car powered by fuel cells with a range of 400 km requires about 4 kg of hydrogen [26], which can be produced by 36 kg of aluminum with the aluminum–water reaction assuming a conversion yield of 100%. Such an on-demand supply system only occupies a volume less than 50 L and costs around US$ 86 based on the current price of US$ 2.4/kg for primary aluminum [27]. In comparison, at least a 225 L-tank with a cost of US$ 1800 are needed to feed such a car if hydrogen is stored in a conventional high-pressure tank operating at 200 bar [26,28]. The potential use of the aluminum-based hydrogen supply system in portable electronics such as laptops has also been reported [29].

For aluminum used as a battery electrode, there is a series of demanding requirements. An ideal material for electrode should be able to offer a high cell voltage while undergoing little corrosion. Presently, high purity aluminum or specially doped aluminum alloys are adopted to satisfy such requirements. In contrast, for hydrogen production, no particular restriction is imposed on aluminum materials used. Even erodible materials are preferred in this process. Thin or heavily adulterated scrap aluminum which is not suitable for recycle for secondary aluminum production can be consumed for hydrogen generation. Therefore, the cost of aluminum-based hydrogen production is potentially low.

4. Hydrogen production from aluminum–water reactions

4.1. Aluminum–water reaction with assistance of alkalis

Hydroxide ions (OH^-) in strongly alkaline solutions are able to destroy the protective oxide layer on the aluminum surface forming AlO_2^-. Therefore, aluminum and its alloys are readily dissolved in the alkaline environment even at room temperature, resulting in hydrogen production. Among different alkalis, sodium hydroxide (NaOH) is the most commonly encountered alkali with the following series of reactions:

$$2Al + 6H_2O + 2NaOH \rightarrow 2NaAl(OH)_4 + 3H_2 \quad (1)$$

$$NaAl(OH)_4 \rightarrow NaOH + Al(OH)_3 \quad (2)$$

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \quad (3)$$

The two steps, shown in the equations above, were suggested to be involved in this hydrogen generation process [25,30–31]. NaOH depleted for the hydrogen evolution in step (1) will be regenerated through the $NaAl(OH)_4$ decomposition in step (2). Therefore, essentially, only water is consumed during the whole process if the reaction is properly controlled. Adding steps (1) and (2) together yields the overall reaction as expressed by Eq. (3). Although it is a well-known parasitic reaction, which is undesirable in alkaline–aluminum–air batteries, this reaction indeed provides a compact source of hydrogen. So far, a number of hydrogen generation devices have been developed based on this reaction [32–40]. Nevertheless, producing hydrogen using this reaction has its disadvantage that NaOH is extremely corrosive and not suitable for hydrogen production for the use in vehicles or in household power systems [37].

The kinetics of the aluminum–water reaction with the addition of NaOH has been extensively studied. Reported activation energy for this reaction is in the range of 42.5–68.4 kJ/mol [25,41–43]. The effects of various parameters on the hydrogen evolution behavior via this method have been evaluated in numerous studies in order to optimize its reaction

conditions. An optimum temperature of 70–90 °C and optimum NaOH concentration of 5.75 M were given by early investigators [44], in whose study the optimum temperature was defined as the temperature at which a high rate of hydrogen production was achieved in a controllable manner, and the optimum alkali concentration was thought as the concentration which minimizes the mass of NaOH and H_2O required for the generation of hydrogen. However, besides temperature and alkali concentration, there are many other factors affecting the hydrogen production performance, including the morphology and initial amount of the metal, concentrations of aluminate ions, metal pretreatments as well as mixing conditions in the reactor [41,45]. If aluminum alloys are used, the alloy compositions will be the key factor to the hydrogen yield [45]. The following results were found from a comprehensive parametric study by Aleksandrov et al. [41]:

(i) the maximum reaction rate was linearly dependent on the initial metal weight for metal powder, while the steady-state reaction rate was a linear function of the surface area for metal foil;
(ii) high concentrations of aluminate ions would inhibit the hydrogen liberation;
(iii) polishing of the metal sample, which promotes the removal of the oxide layer on the metal surface, was able to shorten the induction period, i.e. the time required for the reaction to achieve a steady-state level;
(iv) stirring rates, in contrast, had an insignificant effect on the reaction.

Alloy composition effects were discussed in another work [45] and Al/Si alloy was found to show the highest initial hydrogen generation rate in 16 tested alloy types.

Martınez et al. [18] studied the influences of NaOH/Al molar ratio on hydrogen production at a constant temperature (23 ± 3 °C) directly using soft drink aluminum can wastes. It was observed that with the same amount of aluminum, the higher the NaOH/Al molar ratio, the higher the initial hydrogen liberation rate, but the total volumes of hydrogen produced at the molar ratios of 2.00 and 3.00 were found to be the same. Soon after, Martınez et al. [46] extended their work by coupling an aluminum can-based hydrogen production setup with a proton exchange membrane fuel cell (PEMFC). A proton exchange membrane electrolyzer (PEME) driven by solar energy was also installed in their experiment for comparisons. It was concluded that aluminum cans have a better performance.

In addition to NaOH, other hydroxides were used as the reacting base for hydrogen production [31,45]. In potassium hydroxide (KOH) solution, a synergistic effect on the hydrogen liberation performance was found to be achieved by increasing temperature and base concentration at the same time [31]. Unfortunately, there was a consumption of KOH due to its reaction with CO_2 in the air, which decreased the reaction rate [31]. A recent study [45] compared the hydrogen generation performances with three different hydroxides: NaOH, KOH, and $Ca(OH)_2$. Faster aluminum consumption in NaOH solution was found.

Other than using aluminum or its alloys alone, combining sodium borohydride ($NaBH_4$) with aluminum (or aluminum alloys) in alkaline solutions was proved to be able to enhance both hydrogen production rate and conversion yield [47]. Such enhancement was attributed to both the pH increase caused by the hydrolysis of $NaBH_4$ and the catalytic effects of some aluminum alloys on the hydrolysis of $NaBH_4$ [47]. However, $NaBH_4$, a complex hydride made from borax, is quite expensive for hydrogen production. The results of some selected studies on hydrogen production via the reaction of aluminum or its alloys with water in alkaline conditions are summarized in Table 1.

4.2. Aluminum–water reaction in neutral condition

Aluminum can directly react with water without the help of alkalis:

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \tag{4}$$

Calculated from the above equation, the theoretical hydrogen yield of this reaction for the mixture of aluminum and water in stoichiometric ratios is only 3.7 wt.% but still higher than that of other metals, such as Mg and Zn (3.3 wt.% and 2.4 wt.%, respectively). If water produced from the driven fuel cell is supposed to be fully recovered for the above reaction, its theoretical hydrogen yield will increase to 5.6 wt.%, approaching the target of 6.0 wt.% for hydrogen storage systems set by the U.S. Department of Energy [48].

In comparison with those reactions assisted by alkalis, this method is much safer, but the surface passivation in neutral water occurs much more easily and the metal activity with water is extremely low. Thus, improving the aluminum activity in water can be an essential task for this scenario. Freshly exposed metal surface possesses a relatively higher chemical activity. The release of hydrogen gas was observed through cutting, drilling, or grinding of aluminum and its alloys in water, by which the fresh metal surface was kept exposed in water [49]. The highest volume of hydrogen generated per unit volume of metal removal was found in the case of grinding. However, the reaction stopped immediately after the machining stopped due to the rapid passivation of metal surface [49]. To facilitate continuous generation of hydrogen, metal particles with small sizes, which increase the specific exposed surface area of metals, are favorable [50,51]. One way to produce fine metal powders is the high-energy ball milling, a process in which materials are fractured into small powders under the action of the ball-powder collisions. The size reduction induced by ball milling strongly depends on the mechanical properties of metals [15,52]. Moreover, the milling time needs to be properly controlled since prolonged milling will cause decreases in the powder surface area and the oxidation of powders, both of which increase the corrosion resistance of metals and therefore inhibit the reaction of metal with water [15,52–55]. In addition to its effects on particle sizes, ball milling induces pitting corrosion process by creating numerous

Table 1
Investigations on hydrogen production via the reaction of aluminum (aluminum alloys) in alkaline solutions

Metal/metal alloy	Alkaline solution	Treatment	Temperature (°C)	Maximum hydrogen generation rate	Maximum hydrogen conversion yield[a]	References
Al cans (strip)	NaOH (6.0 M)	Removal of the paint and plastic cover	23 ± 3	12.5 ml/min g	–	[18]
Al (99% purity) (powder)	NaOH (5 M)	–	18.2–60.2	–	–	[25]
Al (99.8%, 99.99% purity); Al–12%Si	NaOH (10 M, 1 M, 0.1 M)	Atomization	25	>500 ml/min/0.2 g	100%	[30]
Al (powder)	KOH (0.1–5 M)	–	70–80	260 ml/min	–	[31]
Al (99.9% purity) (powder)	NaOH (1.0 M, 5.0 M)	–	Room temperature	–	–	[40]
Al (99.7% purity) (foil/powder)	NaOH (0.003–0.1N)	–	30–80	For Al foil, 40 ml/s/cm^2; for Al powder, 6.3 ml/s g of Al	For Al foil, 0.6 μm/1 mm	[41]
Ni–Al alloys (powder)	NaOH (0.2310–0.6931 M)	Rapidly quench	20–60	–	–	[42]
Al alloys with different compositions (powder, rod, bar, foil, tube, plate, flake)	NaOH, KOH, $Ca(OH)_2$	–	25–75	216 ml/min g for Al88/Si12 alloy	76% for Al88/Si12 alloy	[45]
Al, Al/Si, Al/Co, Al/Mg (powder, flake)	NaOH, KOH, $Ca(OH)_2$	Addition of $NaBH_4$	75	190 ml/min g for Al/Si + $NaBH_4$ combination in saturated $Ca(OH)_2$	94% for Al/Si + $NaBH_4$ combination in saturated $Ca(OH)_2$	[47]

[a] Conversion yield is defined as the volume of hydrogen produced over the theoretical volume of hydrogen that should be released assuming that all material is consumed.

defects and fresh surfaces on metals [15,52,55]. However, some storage difficulties may arise as the fine powders are readily oxidized in air.

As a supplement to the mechanical activation of aluminum, the chemical activation effectively improves the aluminum activity by modifying the composition of aluminum alloys. So far, considerable works have been carried out on chemical activation of aluminum alloy anodes, which are widely used in both batteries and sacrificial protection [56–61]. Proposed mechanisms for the aluminum activation with different alloying elements mainly include metal dissolution–deposition process and point defect formation. The theory of metal dissolution–deposition was firstly advanced by Reboul et al. [62], who explained that alloying elements cathodic versus aluminum, such as Zn, Sn, In, and Hg, dissolved in the electrolyte accompanying the anode dissolution would then plate back onto the aluminum surface. Such plating process would locally separate the covered oxide film and therefore it would drive the aluminum potential towards the more active direction. Regarding point defect formation, a localized de-filming process is attributed to the retention and agglomeration of high mobile metallic species on the alloy surface [63]. For the aluminum alloys used for hydrogen production, the activation effects of some elements with low melting point including Zn, Ga and Bi were studied and some encouraging results were reported [19,55]. Mechanical alloying by ball milling can avoid the unnecessary vaporization loss of low-melting-point metals during the alloying process. It also avoids air pollution and creates more defects on the alloy surface [55]. Fan et al. [55] have shown that mechanical alloying by ball milling is a better method to synthesize aluminum alloys for hydrogen production compared with the melting methods. Based on an evaluation of different elements including Zn, Ca, Ga, Bi, Mg, In and Sn, the composition of mechanically synthesized alloys has been optimized for Bi, Zn, Ga, CaH_2, and Al to obtain an initial hydrogen generation rate of 600 ml/min and theoretic conversion yield [55]. However, the use of these particular alloys has obvious drawbacks that these alloys are not readily available and are unstable. Their chemical activity can only be well retained upon storage at liquid nitrogen temperature [19]. On the other hand, Al–salt composites also have been found to display high hydrolysis activity due to the particle size decrease controlled by the salt additives during fabrication as well as the solution temperature increase induced by exothermic dissolution of the salts [16,29,64,65].

Another widely used strategy to enhance the hydrogen generation is to form a corrosion cell by coupling two or more dissimilar metals or metal alloys together in the presence of electrolytes [15,52,66–69]. In the corrosion cell, the dissolution of anode metal will be accentuated by electrochemical corrosion while the hydrogen evolution occurs at the cathodic side. A cathodic material with lower hydrogen overpotential, such as Pt, is therefore preferable for the production of hydrogen [70]. Besides the electrode material, Shifler [71] stated the other factors affecting the performance of a corrosion cell, including effective area ratio of the anodic and cathodic members of the galvanic couple, geometry of the coupling

Table 2
Recent studies on hydrogen production from the reaction of aluminum (or aluminum alloys) with water in neutral conditions

Metal/metal alloy	Treatment	Temperature (°C)	Maximum hydrogen generation rate	Maximum hydrogen conversion yield[a]	References
Al alloys with different compositions	Melting	82	1000 ml/g in ~0.5 h for Al–80 wt.% Ga–5.3 wt.% In–2.0 wt.% Sn–5.4 wt.% Zn–7.3 wt.% alloy	100%	[19]
Al, Al/SiC (block)	Wet cutting/ grinding/drilling	25, 85	–	–	[49]
Al alloys with different compositions (powder)	Ball milling	Room temperature	600 ml/min	100%	[55]
Al–Bi–hydride, Al–Bi–solid salt (powder)	Ball milling	Room temperature	1050 ml/g in 5 min of hydrolysis for 5 h milled Al–10 wt.% Bi–10 wt.% MgH_2 mixture and Al–10 wt.% Bi–10 wt.% $MgCl_2$ mixture	93.4% for 5 h milled Al–10 wt.% Bi–10 wt.% MgH_2 mixture and Al–10 wt.% Bi–10 wt.% $MgCl_2$ mixture	[65]

[a] Conversion yield is defined as the volume of hydrogen produced over the theoretical volume of hydrogen that should be released assuming that all material is consumed.

members, mass transport, bulk solution properties, temperature, flow rate, volume of solution, joint type, surface condition, protective film characteristics in the given environment, and the potential difference between the coupling members. The effects of various parameters on the hydrogen evolution in corrosion cells were investigated using Mg–Pt and Mg–Cu couples by Cho et al. [14]. For aluminum and its alloys, hydrogen coevolution at anode induced by the self-corrosion of aluminum-based materials cannot be neglected. The formation of a passive hydroxide layer on the reactive metal surface causing poor contact between coupling members was considered as the main reason for the rapid interruption of the electrochemical hydrogen generation [15,17,52]. To overcome this problem, Uan et al. [17] devised a setup in which a Pt-coated net was ground onto the Mg sample surface to remove the passive layer. Within their testing period of 8100 s, no significant decrease in the reaction rate was observed [17]. For comparison, some studies on the reaction of aluminum or its alloys with neutral water for hydrogen generation are summarized in Table 2.

4.3. Aluminum–water reaction at elevated temperatures

Besides the above-mentioned aluminum corrosion reactions in water under mild conditions, the mixture of aluminum and water vapor can react (burn) at high temperature and pressure, leading to the following reaction [72,73]:

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2 \qquad (5)$$

This reaction has received much attention due to its possible application in propulsion systems [73,74]. To facilitate this reaction, nano-scale aluminum with high chemical activity, comparable to alkaline metals, was adopted [72,75]. Also, some water-soluble polymers, such as polyacrylamide, were added into water to inhibit the water evaporation during the combustion process and to allow the reaction to take place in a regime of layer-by-layer combustion [72,75]. Recent studies [76–78] indicated that this highly exothermic combustion reaction (heat release of 15.4 MJ/kg) was capable of enhancing hydrogen production from $NaBH_4$ hydrolysis without the need of precious metal catalysts. Through combustion of $NaBH_4/Al/H_2O$ mixtures, a hydrogen generation efficiency of 74–77% and hydrogen yield of ~7 wt.% were obtained [76,78], compared with the practical hydrogen yield of ~5 wt.% for hydrolyzing $NaBH_4$ alone [79].

5. Hydrogen production from aluminum–alcohol reactions

Hydrogen gas can also be produced by reaction of aluminum (or its alloys) with an alcohol activated by I_2, $HgCl_2$, or $SnCl_4$ under refluxing conditions. These reactions have been extensively studied for the synthesis of aluminum alkoxides. The reaction can be described as follows [80]:

$$2Al + 6ROH\,(excess) \xrightarrow{\Delta} 2Al(OR)_3 + 3H_2 \qquad (6)$$

where R can be primary, secondary, or tertiary alkyl groups. One problem associated with this method is to separate the hydrogen gas from a mixture of vapors including alcohols and catalysts.

Alcoholysis of Mg-based materials for hydrogen production was investigated by Grosjean et al. [81]. A maximum reaction conversion yield of 70% was obtained through the decomposition of composite Mg–10 wt.% Ni milled for 30 min in methanol solution [81]. At present, however, no evaluation on the hydrogen evolution characteristics of the alcoholysis of aluminum or its alloys is available.

6. Concept of cogeneration of hydrogen and electrical energy

As mentioned before, aluminum has been a very attractive material for battery anodes for a long time. Among a wide variety of aluminum batteries, the aluminum–air battery was considered to be the best choice for powering vehicles [20,22,82,83]. However, one severe problem involved in aluminum–air batteries is that a parasitic reaction, expressed by Eqs. (1)–(3), will occur at the anode accompanying the current-generating reaction, which greatly reduces the cou-

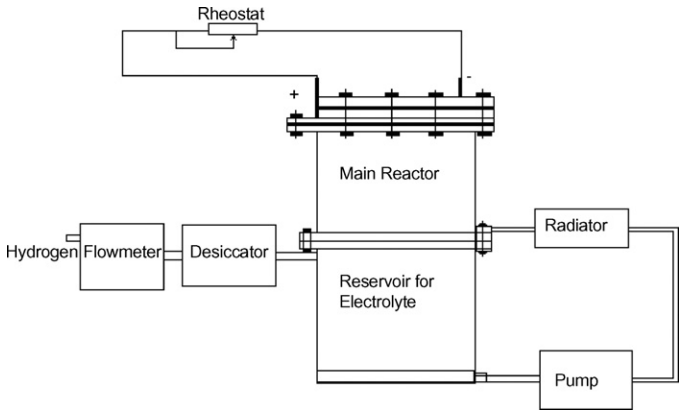


Fig. 1. Structure of aluminum–water hydrogen generator system [89].

lombic efficiency of the batteries. Efforts to suppress this undesired reaction mainly focus on the following two aspects: (i) use of high purity aluminum or aluminum alloys doped with particular elements and (ii) addition of corrosion inhibitors into the electrolyte [84]. Nevertheless, both above-mentioned approaches significantly increase the battery costs.

Contrarily, Zhuk et al. [43] proposed to positively utilize this reaction as a method for hydrogen production rather than suppressing it. The feasibility of this idea was supported by the calculations based on their experimental data. The results indicated that in a combined system, the energy efficiency of commercial grade aluminum alloys, which are more susceptible to parasitic corrosion, is comparable to that of the special anode alloys if the energy stored in the released hydrogen is also taken into account [43,85].

An alternative strategy for the cogeneration of electrical power and hydrogen is to replace the oxygen diffusion cathode in the aluminum-air battery with a hydrogen-evolution cathode [86–89]. In recent studies on this strategy, neutral NaCl solution has been selected as the electrolyte [86–89]. For this strategy, hydrogen is mainly generated from the cathodic reaction while the self-corrosion reaction at the anode contributes a little. The structure of such a combined system designed by Zhang et al. [89] is shown in Fig. 1. The system design is composed of a reactor, a reservoir for electrolyte, as well as systems for the electrolyte circulation and hydrogen flow rate control. A number of aluminum–water cell units, which can be mechanically charged, are connected together in series or parallel within the main reactor to satisfy certain electrical output requirements. The reservoir under the main reactor stores the electrolyte when the system is in its stand-by mode. While under the operating mode, the electrolyte will be pumped into the main reactor from the reservoir to initiate the reaction by contacting the electrodes, and the spare space in the reservoir will be used for hydrogen collection. Excessive electrolyte in the main reactor will then flow back into the reservoir through an outlet on the top of the reactor. Such an electrolyte circulation also helps to remove both the precipitated $Al(OH)_3$ and heat generated during the reaction. The control of hydrogen output rate is accomplished by adjusting the discharging current density of the battery using an external rheostat. Through a series of tests on a system with the structure depicted in Fig. 1 using Ni nets as the cathodes, a maximum open-circuit voltage of 19.8 V and maximum short-circuit current of 7.8 A were reported [87]. Within the testing period of 180 min, the system produced a stable power supply at a voltage of 0.45 V and a current of 7.5 A while the hydrogen generation rate was maintained at 1.0 L/min and above [87]. Since the hydrogen generation characteristics as well as the battery performance of a combined system largely depend on the cathode activity, much attention has been directed toward the synthesis of new cathode materials with high electro-catalytic activity at low costs [88,90].

Since combining the production of hydrogen and electricity in a single system is a relatively newly developed idea, existing investigations on this topic are far from sufficient. For instance, the interaction between the two production processes has not been well understood yet. Presently, the known effects of hydrogen bubbles on the battery performance include an increase of the ohmic overpotential by lowering the conductivity of the electrolyte solution as well as an alteration of the mass-transfer coefficient by enhancing the microconvection and mixing of the solution near the electrode [91]. On the other hand, the hydrogen generation efficiency was found to be related to the current passing through the circuit [92]. Additional studies are required to further develop this idea.

7. Conclusions

Aluminum and its alloys are rather useful for hydrogen production. The high activity of aluminum makes it able to extract hydrogen from different sources including water and hydrocarbons. Of various available reactions, aluminum–water reactions under either alkaline or neutral conditions are most commonly used, while relatively less concern has been put on metal combustion and metal–alcohol reactions. Presently, metal surface passivation remains the major hurdle despite considerable efforts made to overcome this problem. Although a theoretic hydrogen conversion yield is achievable with the help of some arduous treatments such as ball milling and special metal doping, additional research is still needed to further increase the cost effectiveness and fully utilize the energy stored in aluminum-based materials. Inspired by aluminum batteries, systems for cogeneration of hydrogen and electrical energy were proposed. Its feasibility, however, still needs to be further examined. With continuous research and development, aluminum and its alloys will play an important role in hydrogen production.

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